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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C01B 31/02	A1	(11) International Publication Number: WO 00/17102 (43) International Publication Date: 30 March 2000 (30.03.00)
<p>(21) International Application Number: PCT/US99/21367</p> <p>(22) International Filing Date: 17 September 1999 (17.09.99)</p> <p>(30) Priority Data: 60/101,093 18 September 1998 (18.09.98) US</p> <p>(71) Applicant (for all designated States except US): WILLIAM MARSH RICE UNIVERSITY [US/US]; 6100 Main Street, Houston, TX 77843 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): SMALLEY, Richard, E. [US/US]; 1816 Bolsver Street, Houston, TX 77005 (US). HAFNER, Jason, H. [US/US]; 373 Highland Avenue, No. 203, Somerville, MA 02144 (US). COLBERT, Daniel, T. [US/US]; 1911 Milfor Street, Houston, TX 77081 (US). SMITH, Ken [US/US]; 17431 Fairway Oaks, Spring, TX 77379 (US).</p> <p>(74) Agents: POSORSKE, Laurence, H. et al.; Baker & Botts, L.L.P., The Warner, 1299 Pennsylvania Avenue, N.W., Washington, DC 20004-2400 (US).</p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: CATALYTIC GROWTH OF SINGLE-WALL CARBON NANOTUBES FROM METAL PARTICLES</p> <p>(57) Abstract</p> <p>Single-walled carbon nanotubes have been synthesized by the catalytic decomposition of both carbon monoxide and ethylene over a supported metal catalyst known to produce larger multi-walled nanotubes. Under certain conditions, there is no termination of nanotube growth, and production appears to be limited only by the diffusion of reactant gas through the product nanotube mat that covers the catalyst. The present invention concerns a catalyst-substrate system which promotes the growth of nanotubes that are predominantly single-walled tubes in a specific size range, rather than the large irregular-sized multi-walled carbon fibrils that are known to grow from supported catalysts. With development of the supported catalyst system to provide an effective means for production of single-wall nanotubes, and further development of the catalyst geometry to overcome the diffusion limitation, the present invention will allow bulk catalytic production of predominantly single-wall carbon nanotubes from metal catalysts located on a catalyst supporting surface.</p> <div data-bbox="769 1157 1398 1797"> </div>		

CATALYTIC GROWTH OF SINGLE-WALL CARBON NANOTUBES FROM METAL PARTICLES

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention relates generally to methods of producing single-wall carbon nanotubes, and to catalysts for use in such methods.

2. Description of Related Art

10 Fullerenes are closed-cage molecules composed entirely of sp^2 -hybridized carbons, arranged in hexagons and pentagons. Fullerenes (e.g., C₆₀) were first identified as closed spheroidal cages produced by condensation from vaporized carbon.

Fullerene tubes are produced in carbon deposits on the cathode in carbon arc methods of producing spheroidal fullerenes from vaporized carbon.
15 Ebbesen et al. (Ebbesen I), "Large-Scale Synthesis Of Carbon Nanotubes," Nature, Vol. 358, p. 220 (July 16, 1992) and Ebbesen et al., (Ebbesen II), "Carbon Nanotubes," Annual Review of Materials Science, Vol. 24, p. 235 (1994). Such tubes are referred to herein as carbon nanotubes. Many of the carbon nanotubes made by these processes were multi-wall nanotubes, i.e., the carbon nanotubes
20 resembled concentric cylinders. Carbon nanotubes having multiple walls have been described in the prior art. Ebbesen II; Iijima et al., "Helical Microtubules Of Graphitic Carbon," Nature, Vol. 354, p. 56 (November 7, 1991).

Another known way to synthesize nanotubes is by catalytic decomposition of a carbon-containing gas by nanometer-scale metal particles
25 supported on a substrate. The carbon feedstock molecules decompose on the particle surface, and the resulting carbon atoms then diffuse through the particle and precipitate as part of nanotubes growing from one side of the particle. This procedure typically produces imperfect multi-walled nanotubes in high yield. See C. E. Snyder et al., International Patent Application WO 89/07163 (1989), hereby
30 incorporated by reference in its entirety. Its advantage is that it is relatively simple and can be scaled to produce nanotubes by the kilogram.

nickel, cobalt, or a mixture thereof, to produce single-wall carbon nanotubes in yields of at least 50% of the condensed carbon. See A. Thess et al. (1996), *Science* 273:483. The single-wall nanotubes produced by this method tend to be formed in clusters, termed "ropes," of 10 to 1000 single-wall carbon nanotubes in parallel alignment, held together by van der Waals forces in a closely packed triangular lattice. Nanotubes produced by this method vary in structure, although one structure tends to predominate. These high quality samples have for the first time enabled experimental confirmation of the structurally dependent properties predicted for carbon nanotubes. See J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, C Dekker (1998), *Nature*, 391:59; T. W. Odom, J. L. Huang, P. Kim, C. M. Lieber (1998), *Nature*, 391:62.

Although the laser vaporization process produces improved single-wall nanotube preparations, the product is still heterogeneous, and the nanotubes are too tangled for many potential uses of these materials. In addition, the vaporization of carbon is a high-energy process and is inherently costly. Therefore, there remains a need for improved methods of producing single-wall nanotubes of greater purity and homogeneity. Furthermore, applications could make use of the properties of single-wall carbon nanotubes if only they were available in a form where they were attached directly to the surface of a macroscopic object. However, such components have not been produced up to now.

A method of producing carbon fibers from single-wall carbon nanotubes is described in PCT Patent Application No. PCT/US98/04513, incorporated herein by reference in its entirety. The single-wall nanotube molecules are produced in substantially two-dimensional array made up of single-walled nanotubes aggregating (e.g., by van der Waals forces) in substantially parallel orientation to form a monolayer extending in directions substantially perpendicular to the orientation of the individual nanotubes. Such monolayer arrays can be formed by conventional techniques employing "self-assembled monolayers" (SAM) or Langmuir-Blodgett films, see Hirsch, pp. 75-76.

Typically, SAMs are created on a substrate which can be a metal (such as gold, mercury or ITO (indium-tin-oxide)). The molecules of interest, here the single-wall nanotube molecules, are linked (usually covalently) to the substrate

wall nanotubes on the catalyst particles of less than 2-nanometer diameter but is formed into graphitic layers that encapsulate the larger catalyst particles, deactivating them as catalysts. Catalyst particles of greater than about 2 nanometers in diameter are more likely to form multiwall nanotubes, and since they are rendered
5 ineffective by the process, the only remaining active catalyst particles support growth of primarily single-wall nanotubes. In a preferred embodiment, the method of this invention provides for treatment of supported catalyst material to deactivate catalyst particles that do not support growth of the desired nanotube types, with subsequent change of the feedstock composition or density to accelerate growth of
10 the desired form of single-wall nanotubes. The method of this invention is capable of producing material that is >50 % SWNT, more typically >90 % SWNT, or even >99 % SWNT.

This invention also provides a catalyst/support system structured so that access of the feedstock gas to the catalyst is enhanced by that structure.
15 Preferably, the catalyst is deposited so that there is clear distance between catalyst locations by dispersion of small catalyst particles on the substrate surface or other methods of deposition known to those skilled in the art.

The production of high quality single-wall carbon nanotubes, in some cases including double-wall carbon nanotubes, in yields much larger than previously
20 achieved by catalytic decomposition of carbon-containing precursor gases is disclosed. The nanotubes formed are connected to and grow away from the catalyst particles affixed to the catalyst support surface. If the growth time is short, the tubes can be only a fraction of one micron long, but if the growth time is prolonged, single-wall carbon nanotubes in this invention can grow continuously to arbitrary
25 lengths. The present invention demonstrates a means for nucleating and growing nanotubes only from the smallest of the supported catalyst particles, which produce single-wall carbon nanotubes, while deactivating the larger particles so that no multi-walled nanotubes are produced. This allows the growth exclusively of single-wall carbon nanotubes from catalyst systems previously thought to produce only
30 larger diameter multi-walled nanotubes.

According to one embodiment of the present invention, a process for producing single wall carbon nanotubes is disclosed. The process comprises the

Fig. 3 is a TEM image of single-wall carbon nanotube grown at 850°C by 1200 sccm CO over an alumina:Fe:Mo catalyst.

Fig. 4 is a SEM image of nanotube ropes grown at 800°C in 1000 sccm Ar, 0.66 sccm C₂H₄, 0.33 sccm H₂.

5 Fig. 5 is a TEM of the same material that shows ropes that consist of nanotubes of diameter 0.5nm - 3 nm and 1 or 2 walls, respectively.

Fig. 6 is a graph of the energies of capsules and single wall nanotubes relative to an infinite graphene sheet.

DETAILED DESCRIPTION OF THE EMBODIMENTS

10 Carbon has, from its very essence, not only the propensity to self-assemble from a high temperature vapor to form perfect spheroidal closed cages (of which C60 is prototypical), but also (with the aid of a transition metal catalyst) to assemble into perfect single-wall cylindrical tubes. These tubes, which may be thought of as one-dimensional single crystals of carbon, are true fullerene molecules.

15 Single-wall carbon nanotubes are much more likely to be free of defects than multi-wall carbon nanotubes. Defects in single-wall carbon nanotubes are less likely than defects in multi-walled carbon nanotubes because the latter have neighboring walls that provide for easily-formed defect sites via bridges between unsaturated carbon valences in adjacent tube walls. Since single-wall carbon nanotubes have fewer defects, they are stronger, more conductive, and therefore
20 more useful than multi-wall carbon nanotubes of similar diameter.

Carbon nanotubes may have diameters ranging from about 0.6 nanometers (nm) for a single-wall carbon nanotube up to 3nm, 5nm, 10nm, 30nm, 60nm or 100nm for single-wall or multi-wall carbon nanotubes. The carbon
25 nanotubes may range in length from 5nm up to 1 millimeter (mm), 1 centimeter (cm), 3cm, 5cm, or greater. The process described here enables one to produce high quality single-wall carbon nanotubes, and, in some cases double-wall carbon nanotubes, in yields much larger than previously achieved in growth from supported catalysts. The yield of single-wall carbon nanotubes in the product made by this
30 invention is unusually high. Yields of single-wall carbon nanotubes greater than 90% are possible with this invention. This is achieved by nucleating and growing nanotubes from the smallest of the supported catalyst particles, which produce

provide substantially planar surfaces, e.g., flakes. The support may range in size from about 10 nm to centimeters.

Transition Metal Catalyst

A variety of transition metal-containing clusters are suitable as catalysts when used with an appropriate combination of reaction parameters. The transition metal catalyst can be any transition metal that will cause conversion of the carbon-containing feedstock described below into highly mobile carbon radicals that can rearrange at the growing edge to the favored hexagon structure. Suitable materials include transition metals, and particularly the Group VIB chromium (Cr), molybdenum (Mo), tungsten (W) or Group VIIIB transition metals, e.g., iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) or mixtures thereof. Metals from the lanthanide and actinide series may also be used. Preferred are Fe, Ni, Co and mixtures thereof, such as a 50/50 mixture (by weight) of Ni and Co or a mixture of Fe/Ni. Any of these transition metals individually or in combination with any of the other transition metals listed may be used in clusters to serve as a catalyst for single-walled carbon nanotube growth. Particularly preferred catalysts are mixtures of two or more of the listed metals.

The transition metal clusters may have a size from about 0.5 nm to over 30 nm. Clusters in the range of 0.5 to 3 nm will produce single-wall nanotubes, while larger clusters tend to produce multiwall nanotubes with outer diameters greater than about 3 nm. In a preferred mode, the larger clusters are inactivated by the process of this invention, with the result that catalytic production of nanotubes using this preferred catalyst will be predominately single-wall nanotubes. The transition metal clusters may be substantially uniformly dispersed on the support surface in close proximity to one another so that the single-wall nanotubes that grow from the support form bundles or ropes of generally aligned single-wall carbon nanotubes. Alternatively, transition metal clusters may be dispersed on the support surface so that there is clear separation between the clusters, so that the single-wall nanotubes that grow from the support are separate from one another.

Catalysts may be prepared using known methods, and can be (i) prepared in advance in fully active form, (ii) prepared in precursor form followed by

supply to the catalyst, which reduces the carbon concentration in the catalyst particles. A lower carbon concentration will allow the carbon structures to form more slowly, giving each carbon atom more time to anneal to its lowest energetic configuration. The lowest-energy bonded carbon structure on a catalyst particle at
5 least 3 nm in diameter is an encapsulation of the catalyst particle with a graphite-like sheet, while for smaller diameter catalyst particles, the lowest-energy structure is a single-walled nanotube growing the particle.

Lower supply of carbon to the catalyst may be achieved in various ways, depending on the source of gaseous carbon. In the reaction of CO to produce
10 nanotubes, slow carbon supply rate arises because CO decomposition is a bimolecular disproportionation that involves the breaking of two strong CO triple bonds: such a reaction is expected to proceed very slowly except at very high temperatures and pressures much greater than reaction pressure of about 1 atmosphere. The catalytic decomposition of C_2H_4 proceeds quickly at about 1 atm.;
15 however, the reaction can be slowed down by limiting the partial pressure of C_2H_4 to 0.5 Torr.

Reducing the amount of carbon supplied to the catalytic particle may be accomplished by lowering the gas pressure in the reactor, typically by reducing the feed rate into the reactor. Alternatively, the amount of feedstock added to the
20 gas flow may be reduced to reduce the partial pressure of the feedstock gas in the reactor. Generally, the pressure in the reaction zone should be selected, at least initially, to inactive the larger diameter catalyst particles, while favoring the growth of single-wall nanotubes from the smaller diameter catalyst particles. As described above, the partial pressure at which the carbon supply to the catalytic particles is rate
25 limiting will depend on the reaction mechanism. For example, the partial pressure for CO that meets this condition will be much higher than the partial pressure for ethylene. The initial CO pressure may be from about 0.1 Torr to 10 Atmospheres. Preferably, the initial pressure in the reaction zone is 1.2 Atmospheres.

Evidence that there has been a successful change of the rate-limiting
30 step from carbon diffusion through the catalytic particle to carbon supply to the catalytic particle can be found in three aspects of the catalytic system of this invention. First, the product mass increase rate varies linearly with the hydrocarbon

tube furnace. A preferred CO flow rate is about 1200 sccm in a one-inch diameter tube furnace.

Once the larger diameter catalyst particles have been deactivated, the conditions in the reaction zone may be changed to conditions that enhance the production of single-wall carbon nanotubes. This includes increasing the temperature and/or the pressure of CO or changing to another of the carbon-bearing reagent gases mentioned above.

In an alternate embodiment, the conditions in the reaction zone may be selected such that there is no need to change reaction zone conditions to favor the growth of single-wall nanotubes from the smaller diameter catalyst particles after inactivating larger diameter catalyst particles. Conditions initially selected also allow the single-wall nanotubes to remain active under these conditions. For example, the CO pressure in the reaction zone may be from about 500 Torr to about 2000 Torr. The temperature may be from about 600°C to about 900°C. The flow rate of the precursor may be from about 500 to about 2000 sccm in a 1-inch diameter tube furnace.

The yield of single-wall carbon nanotubes may selectively changed by changing the temperature in the reaction zone. The mass yield of SWNT is temperature dependent, with the yield increasing with increasing temperature. Selectivity can also be affected by temperature, with the product mix varying from 30% double wall nanotubes at 700°C to 70% double wall nanotubes at 850°C.

As shown in Figures 1 and 4, both CO disproportionation over Mo catalyst particles at 850°C and the reaction of C_2H_4 with Fe/Mo particles at 700°C appear to generate single-wall carbon nanotubes that grow continuously without termination of the growth reaction. These results constitute the first demonstration of continuous generation of single-wall carbon nanotubes with lengths that are, in principle, arbitrarily long. In practice, however, the mass of the grown nanotubes exhibits a time dependence that is less than linear, so that growth slows more and more with increasing time (a fit of the data sets in Fig. 2 give roughly square root dependencies of yield on time). This slowing growth may be due to the increasing diffusion time of the carbon feedstock molecules through the thickening mat of nanotubes surrounding the catalyst particles.

nanotubes) unless the process is carried out with excess hydrocarbon feedstock. The product of a typical process for making mixtures containing single-wall carbon nanotubes is a tangled felt, which can include deposits of amorphous carbon, graphite, metal compounds (e.g., oxides), spherical fullerenes, catalyst particles
5 (often coated with carbon or fullerenes) and possibly multi-wall carbon nanotubes. The single-wall carbon nanotubes may be aggregated in "ropes" or bundles of essentially parallel nanotubes.

Nanotubes prepared using the catalytic method of this invention tend to be less contaminated with pyrolytic or amorphous carbon than nanotubes prepared
10 by prior art methods. Furthermore, by using a catalyst with a narrow size distribution, the nanotubes produced consequently have a narrow size distribution. This will minimize the need for post-production activities to clean up the nanotube preparation. To the extent that the nanotube product contains pyrolytic carbon which needs to be removed, various procedures are available to the skilled artisan
15 for cleaning up the product. Suitable processes for purifying carbon nanotubes prepared according to this invention include the processes described in International Patent Publication WO 98/39250.

According to the invention, predominantly single-wall carbon nanotubes, with a portion of double-wall carbon nanotubes under some conditions,
20 are produced with diameters in the range from about 0.5 to about 3 nm. Typically, no 5 to 20 nm diameter multi-walled nanotubes are produced by supported catalyst particles. The key difference responsible for these effects is that the growth reaction rate is limited by the supply of carbon to the catalyst particles, whereas the multi-walled nanotube growth is thought to be limited by the diffusion of carbon through
25 the catalyst particles.

The single-wall nanotubes of the present invention may have lengths exceeding one micron. The length may be controlled by lengthening or shortening the amount of time the catalyst is exposed to the feedstock gas at an appropriate temperature and pressure. In one embodiment, under proper conditions the single-
30 wall nanotubes can grow continuously to an arbitrary length.

Single-wall nanotubes formed in the present invention are observed to form into organized bundles or "ropes" as they grow from catalyst particles in

In order to facilitate a more complete understanding of the invention, an Example is provided below. However, the scope of the invention is not limited to specific embodiments disclosed in this Example, which is for purposes of illustration only.

5 1. Preparation

Single wall carbon nanotubes may be grown by passing carbon-containing gases (CO or C₂H₄) at elevated temperatures over nanometer-size metal particles supported on larger (10-20 nm) alumina particles. Two different metal catalysts may be used, one containing pure Mo, the other containing Fe and Mo.
10 The ratio of FE to Mo may be 9:1. Both catalysts were made using a method known in the art.

For each growth experiment, a quartz boat containing a carefully weighed amount (typically 20 mg) of the catalyst powder was placed in the center of a 1 inch quartz tube furnace. The system was purged with Ar, then heated under
15 flowing reactant gases to an elevated temperature for a controlled time. The resulting catalyst material, which now also contains reaction products dominated by single-wall carbon nanotubes, was removed from the boat and weighed again. The yield is defined as the mass increase divided by the original catalyst mass. Samples were prepared for TEM imaging by sonicating this material in methanol and drop-
20 drying the resulting suspension onto TEM grids.

2. Production of single-wall carbon nanotubes

The production of single-wall carbon nanotubes by the disproportionation of CO over alumina-supported Mo particles is greatly improved. The catalyst is 34:1 alumina:Mo by mass. The reaction is carried out at 850°C under
25 a flow of 1200 sccm of CO at 900 Torr. The resulting material, which consists of single-wall carbon nanotube very monodisperse in diameter (0.8 to 0.9 nm), is shown in Fig. 1. Particles of the fumed alumina support, 10 to 20 nm in size, are also visible in this and subsequent TEM images. The yield of nanotubes is plotted as a function of reaction time in Fig. 2. The yield continues to increase even for very
30 long reaction times.

CO also forms nanotubes with a second catalyst. The second catalyst is prepared with 90:9:1 alumina:Fe:Mo by mass. The reaction, when carried out

nanotubes grow aligned in large bundles, keeping their growing ends exposed to the gaseous feedstock. Similar modifications to the current technique may allow the bulk production of single-wall carbon nanotubes.

While the invention has been described in connection with preferred
5 embodiments, it will be understood by those skilled in the art that other variations
and modifications of the preferred embodiments described above may be made
without departing from the scope of the invention. Other embodiments will be
apparent to those skilled in the art from a consideration of the specification or
practice of the invention disclosed herein. It is intended that the specification is
10 considered as exemplary only, with the true scope and spirit of the invention being
indicated by the following claims.

8. The method of claim 1, wherein said at least one carbon containing gas is selected from the group consisting of CO, C₂H₄, and combinations thereof.
9. The method of claim 1, wherein said metal particle is selected from the group consisting of Group VIB transition metals, chromium (Cr), molybdenum (Mo), tungsten (W) and Group VIIB transition metals, e.g., iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt) and mixtures comprising any of these.
10. The method of claim 9, wherein said metal particle comprises at least two of the listed metals.
11. The method of claim 1, wherein a lower concentration of carbon in said at least one carbon containing gas allows each carbon atom in said single-wall carbon nanotube sufficient time to anneal to its lowest energetic configuration.
12. The method of claim 1, wherein said support comprises flat alumina flakes.
13. The method of claim 1, wherein said solid catalyst support is porous, permitting passage of said carbon-containing gas therethrough.
14. The method of claim 1 or claim 13, wherein said metal particles were distributed on said support to enhance access of said carbon-containing gas to growing single-wall nanotubes.
15. The method of claim 14, where said metal particles are distributed to provide clear space between particles.

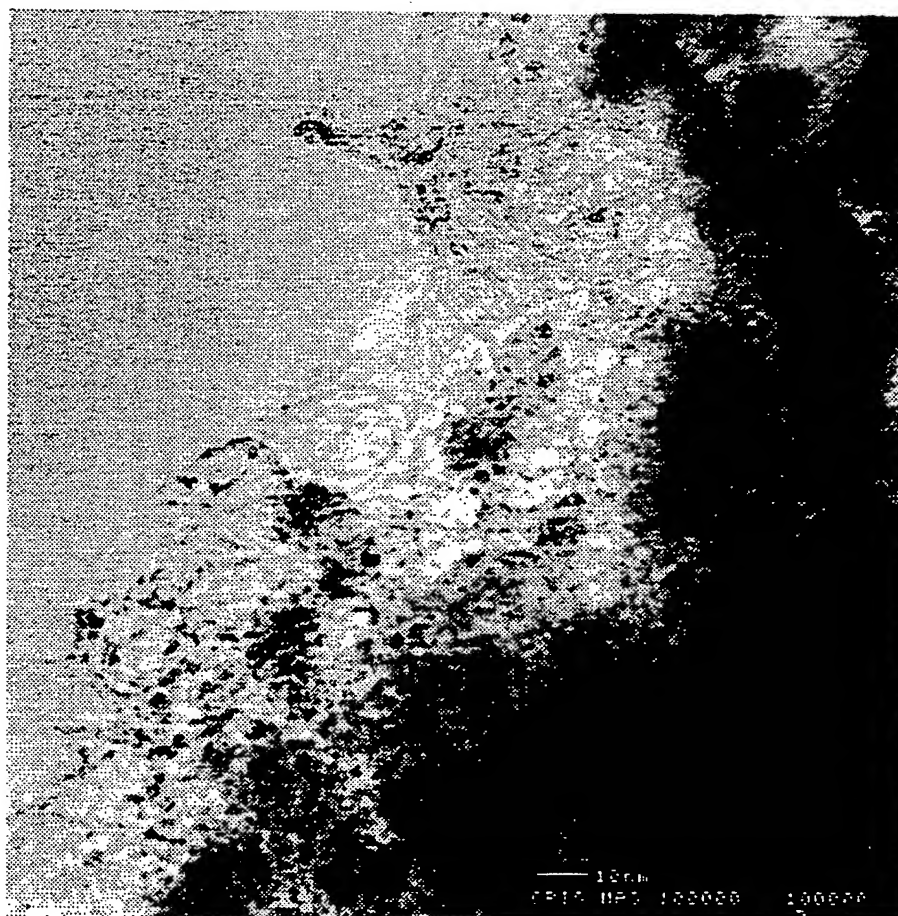


FIG. 1

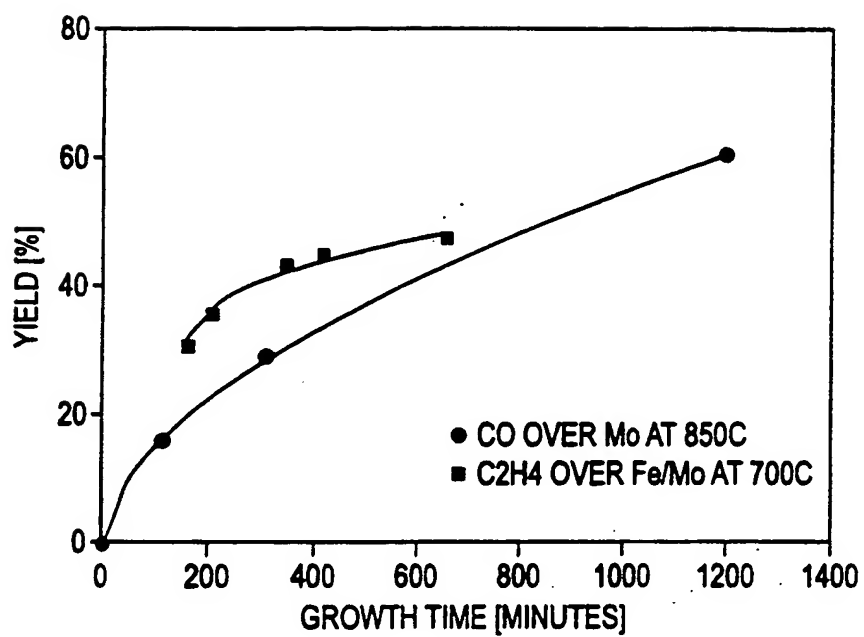


FIG. 2

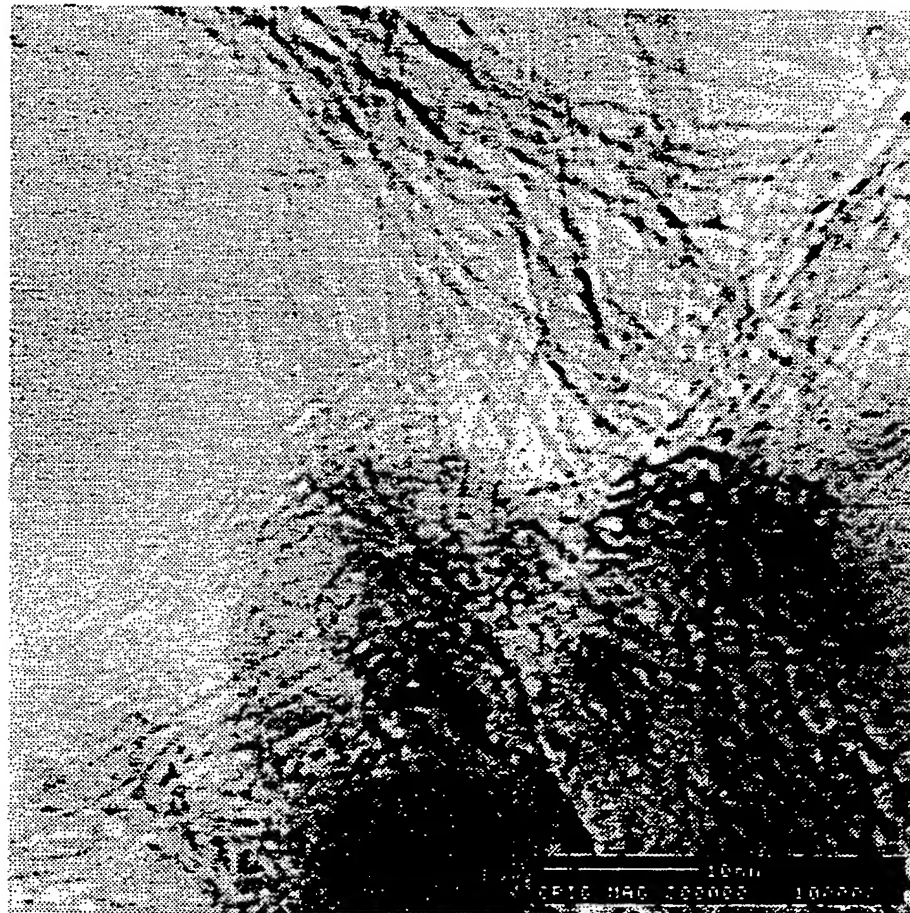


FIG. 3

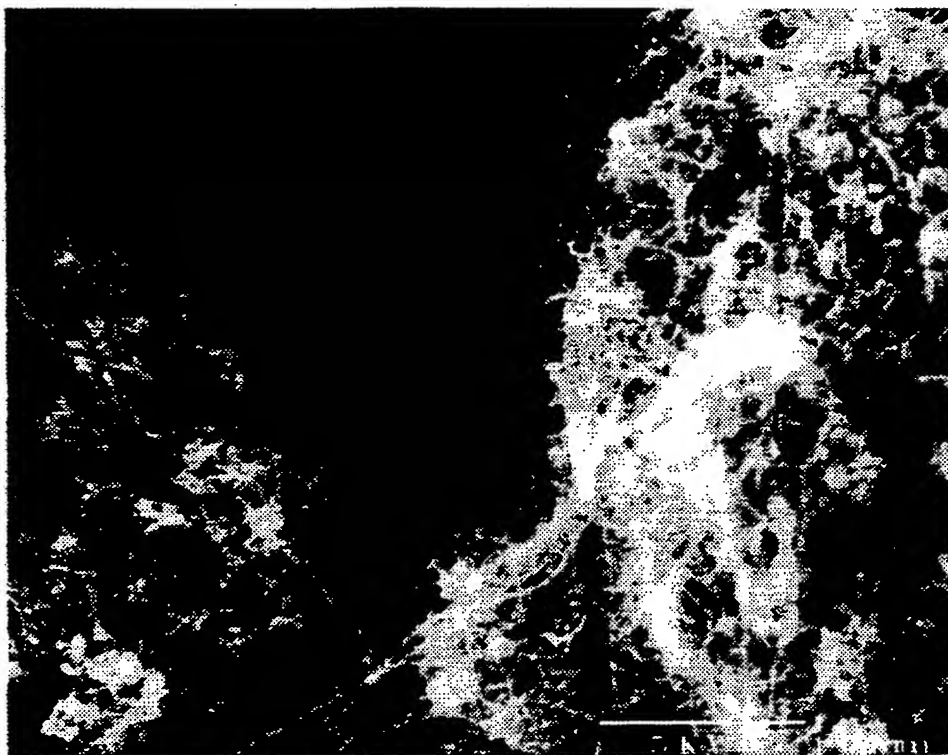


FIG. 4

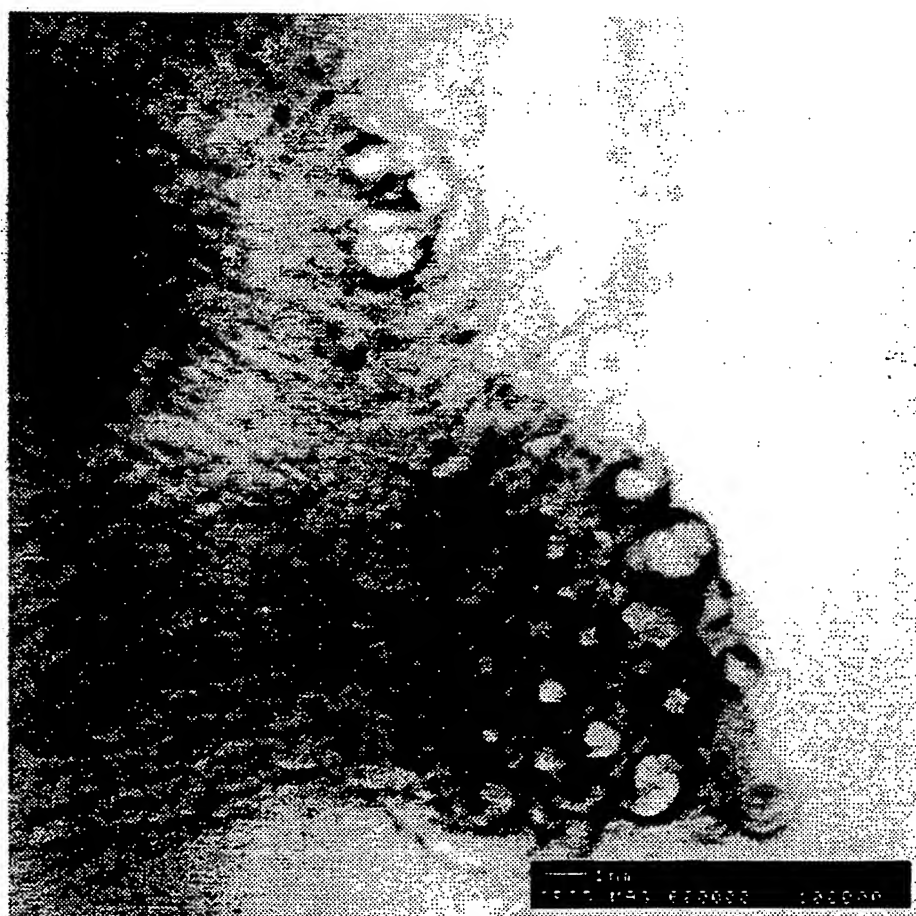


FIG. 5

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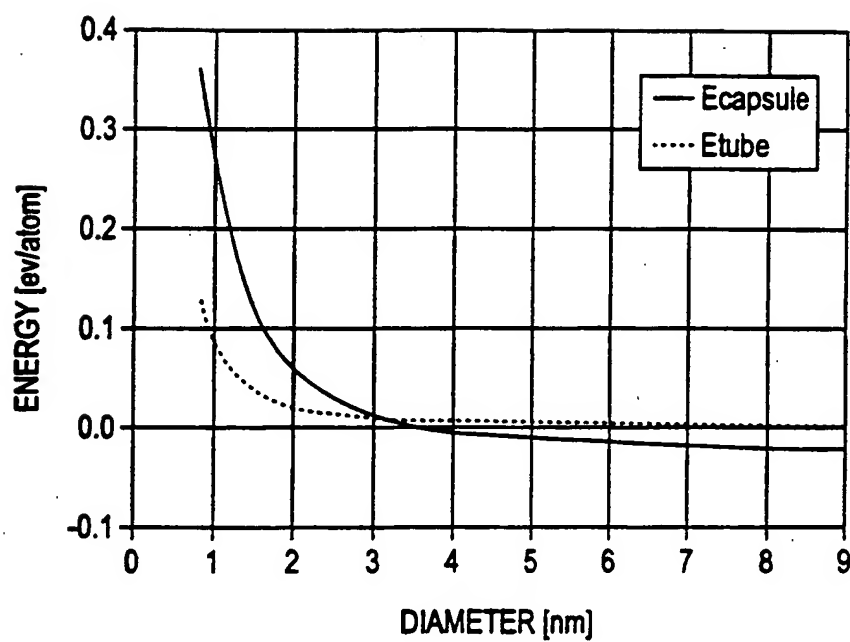


FIG. 6

INTERNATIONAL SEARCH REPORT

In International Application No
PCT/US 99/21367

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	HAFNER J H ET AL: "Catalytic growth of single-wall carbon nanotubes from metal particles" CHEMICAL PHYSICS LETTERS, 30 OCT. 1998, ELSEVIER, NETHERLANDS, vol. 296, no. 1-2, pages 195-202, XP000869784 ISSN: 0009-2614 the whole document -/-	1-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

25 January 2000

Date of mailing of the international search report

04/02/2000

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No.
PCT/US 99/21367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HERNADI K ET AL: "Catalytic synthesis of carbon nanotubes using zeolite support" ZEOLITES,US,ELSEVIER SCIENCE PUBLISHING, vol. 17, no. 5-6, page 416-423 XP004072294 ISSN: 0144-2449</p>	1
A	<p>HERNADI K ET AL: "Fe-catalyzed carbon nanotube formation" CARBON,GB,PERGAMON PRESS. OXFORD, vol. 34, no. 10, page 1249-1257 XP004068885 ISSN: 0008-6223</p>	1
A	<p>WO 97 09272 A (WILLIAM MARSH RICE UNIVERSITY) 13 March 1997 (1997-03-13)</p>	